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Review

Heterothiometallic polymeric clusters

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Contents

Abstract

Heterothiometallic clusters with many fascinating configurations can be prepared by liquid or solid state reaction methods. Cluster units with reactive binding sites can be organized into ordered zero-, one (1D)-, two (2D)- and three (3D)-dimensional structures in which they can act as either electron donors or electron acceptors. This article surveys the skeletal structures, syntheses and reactions of heterothiometallic polymeric clusters currently available emphasizing the polymeric structural features of compounds based on reactive cluster unit construction.

Keywords: Heterothiometallates; Polymeric clusters; Self-assembly; Structural and spectrum properties

1. Introduction

Coordination polymers sustained by coordinate covalent bonds represent one important class of compounds currently being investigated by crystal engineers. These compounds received much attention in the past few years due to their fascinating structures and potentially useful properties for the catalysis, conductivity, and for the creation of microporous and magnetic materials [1]. Of particular interest are transition metal central atoms with different coordination numbers acting as construction junctions for these self-assemblies extended in one, two or three dimensions. Interestingly, if clusters are located at knot positions, a novel species is formed, polymeric clusters (Fig. 1), which are the subject of this paper. As their name implies the nature of these aggregates is an active combination of supramolecular and cluster chemistry, and clusters are involved as fundamental construction units.

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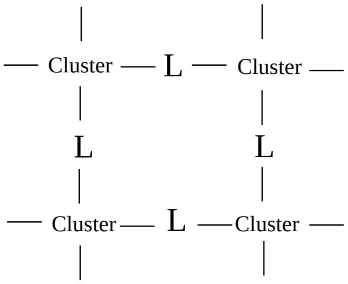


Fig. 1. A scheme of polymeric cluster.

Heterothiometallic clusters form a well-established group due to their importance in catalysis and biological processes (see, for example [2]). An important factor favorable for the development of this subject was the discovery of interesting optical limiting properties of heterothiometallic clusters [3a]. Such transition metal clusters may exhibit both large nonlinear optical effects and low extinction coefficients in the visible region if appropriate constituent elements, oxidation states and cluster structures are selected [3b]. On the basis of this strategy, a series of monomeric thiometallates containing $[MX_nS_{4-n}]^{2-}$ ions (M = Mo, W, Re; X = O, S, Se; $n = 0$–2) have been prepared and studied [4–9]. MS_4^{2-} ions have found widespread use in the syntheses of clusters due to their symmetric structure. They coordinate to the neutral species M′ X (M′ = Cu^+, Ag^+; X = Cl^-, Br^-, I^-, CN^-, NCS^-) to generate diversiform aggregates by means of bi-, tri- or tetradentate coordination. Interestingly, in some cases the halide/pseudohalide ligand X is capable of bridging monomeric cluster units via M′-coordination to form polymeric arrays. It thus became possible to incorporate cluster units into coordination polymers or supramolecular architectures by further nucleophilic substitution, with the ultimate goal of constructing systems with tailor made properties. Although there has been good progress in understanding the nature of the monomeric entities in general, much less is known about the polymeric assemblies that possess the combined strength of clusters and polymers. Thus, a number of important properties and functions can be anticipated.Heterothiometallic polymeric clusters may be categorized into five main groups:

- cluster monomers (abbreviated as **m**),
- zero-dimensional oligomers (abbreviated as **o**),
- one-dimensional (1D) chains (abbreviated as **c**),
- two-dimensional sheets (2D) (abbreviated as **s**), and
- three-dimensional networks (3D) (abbreviated as **n**),

showing three construction elements for such polymeric cluster species: cluster junctions, bridging ligands and construction fashion.

Although one MS_4^{2-} tetrahedron can bind directly M′ or M′X successively with its six S–S edges to a finally heptanuclear cluster unit, because of the bridging effect of X, up to 10 heterometals can be accommodated around the $MS_4{}^{2-}$ moiety (Fig. 2, **m1–15**, The metal–metal bonds and cation moieties or guest molecules are not depicted in most of structural schemes for the reason of clarity). From another point of view, this heterometalization may be considered as a pre-assembly process. It is convenient to regard these monomeric ions as basic construction units, which contain sulfur atoms with lone-pair electrons as donors and the coordinatively unsaturated metal centers as acceptors. Both of these active binding sites possess potential for further assembly with other proper components (via intermolecular coordination). Both skeletal and peripheral ligands may be involved in such a self-assembly process (Fig. 3). In the present case, the skeletal ligands are mainly the chalcogen atoms (S, Se) attached to the core metal M in the inner sphere. The related peripheral ligands include halides, CN^-, NCS^- or some organic multifunctional groups linked to the heterometal M′ in the third sphere. The properties of the cluster units (both electron-acceptor (EA) for heterometals and electron-donor (ED) for chalcogen) render them as active cluster junctions or connectors in the assembly processes, thus producing two kinds of construction mode (such as **c6** and **c20**).

Here, we provide a first comprehensive summary of this novel and rapidly emerging area of chemistry. Particular emphasis is put on the analysis of polymeric frameworks of “electron-deficient” heterothiometallic clusters and on a systematic approach to an understanding of the different polymeric structures. A restriction to the scope of this article is that only structurally regular and crystallographically characterized systems will be covered. Many characteristic construction regularities can be extracted which may provide a possible synthetic methodology for further research. In the latter part, the synthesis for assembly and reactivities for disassembly of polymeric structures is discussed to some extent as two adverse processes.

2. Polymeric cluster species

2.1. Zero-dimensional oligomers

The known cluster monomers **m1–8**, and **m11** undergo an oligomerization process to form discrete assemblies. Some representative examples are presented here (Fig. 4, **o1–9**).

The linear dimer (**o1** [10]) can be regarded as an assembly of monomeric blocks **m1** with heterometals. Other S-bridging examples include the saddle aggregate **o2** [11], the hexagonal prism-shaped dimer **o3** [3b], the mixed-polymerizing cluster **o4** [12], the eight nuclear square **o5** [13], and the eicosanuclear cluster **o6** [14]. The square monomer **m11** share peripheral X bridges to form the dimer **o7** [15], and the nest shaped monomer **m7** partakes the outer iodide bridges to form the dimer **o8** [16]. A similar peripheral ligand-bridging example is the windmill-shaped dimer **o9** [17]. Due to the existence of reactive binding sites around these oligomers these clusters can be regarded as secondary construction units.

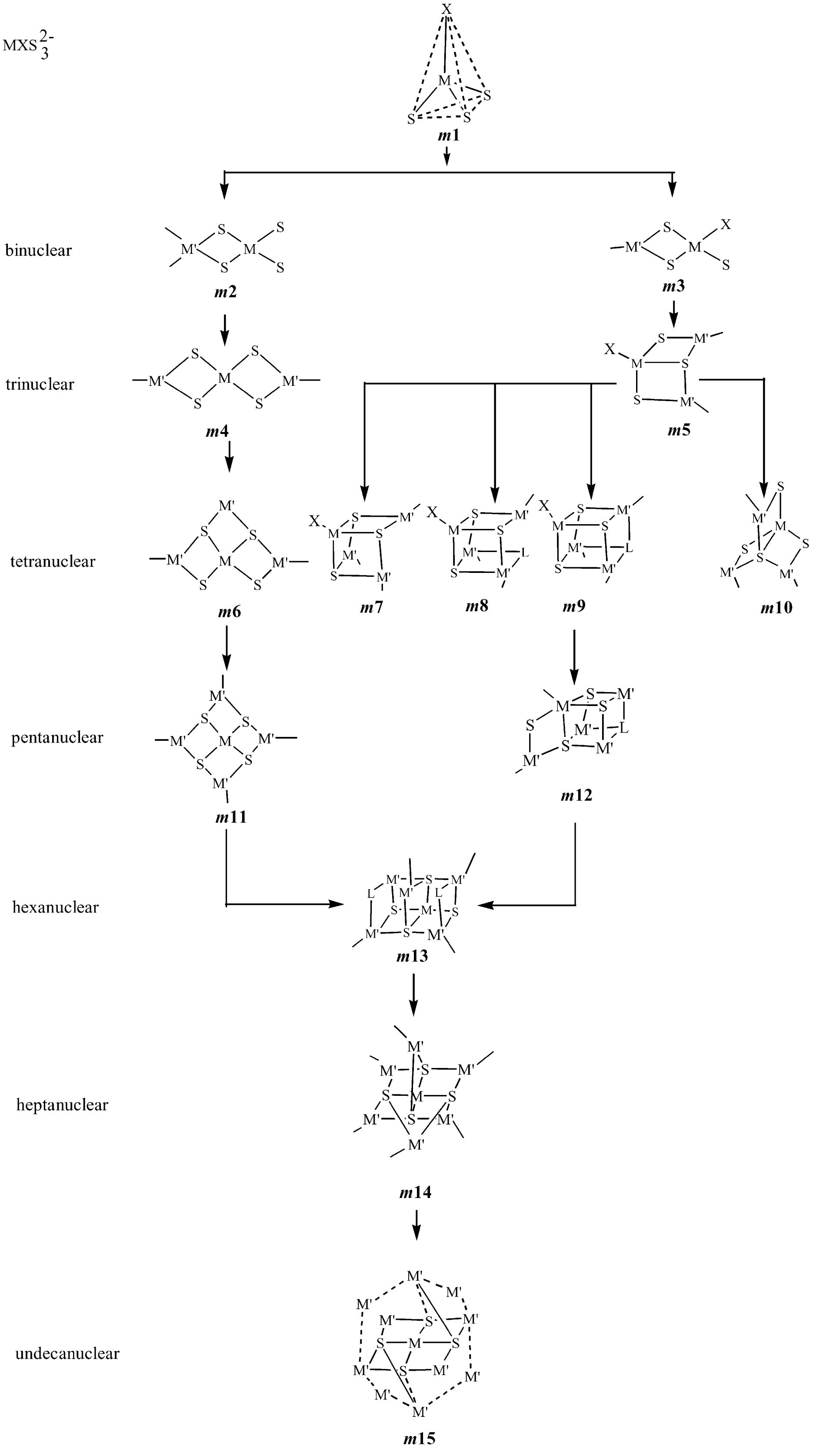


Fig. 2. Fifteen cluster monomers as fundamental building blocks.

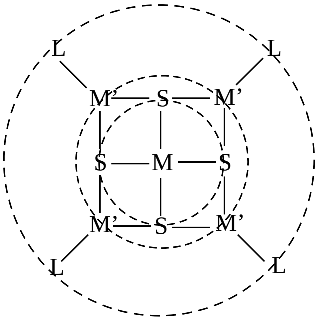


Fig. 3. Coordination spheres in heterothiometallates.

2.2. One-dimensional polymeric clusters

The majority of the known heterothiometallic polymeric clusters possess this type of structural motif. According to their different construction fashion these compounds can be grouped into two classes: peripheral ligand—bridging assemblies and skeletal ligand—bridging assemblies. In the former type cluster units serve as junctions of polymeric frameworks, in the latter cluster units may act as connectors or junctions.

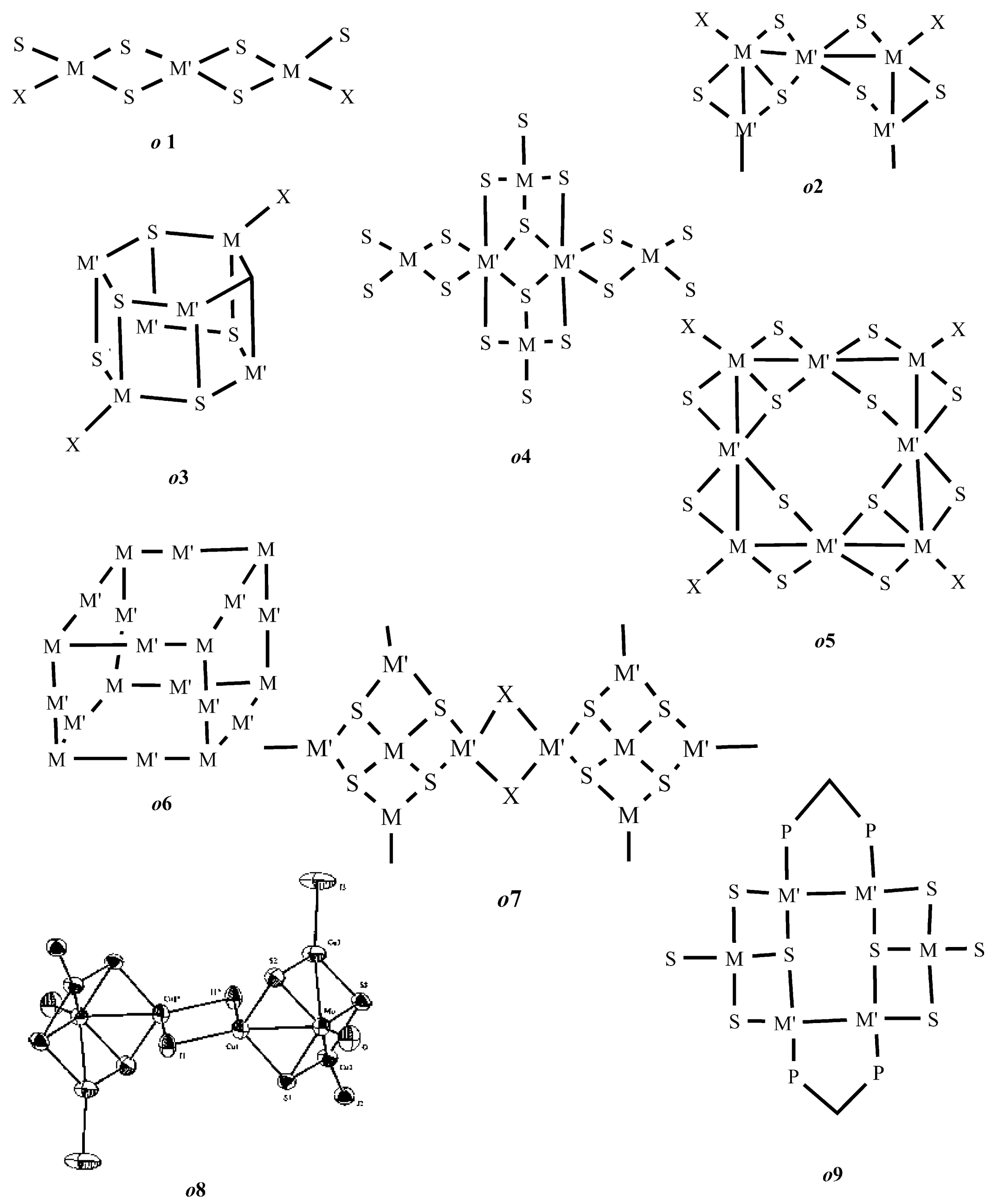


Fig. 4. Nine cluster oligomers as secondary construction blocks.

2.2.1. Peripheral ligand—bridging assemblies

CN^- and halide ligands coordinate to metal atoms either in the terminal (*t*-) or in the bridging (μ-) mode. As far as the thiocyanate anion is concerned, besides the classical coordination type including terminal (*t*-) or bridging modes (μ-), another type of bridging coordination found in polymeric clusters is that of the μ_3-NCS^- with an additional weak M′–SCN interaction.

Among the familiar peripheral ligands, cyano bridges are often accompanied by zigzag structures (Fig. 5, **c1**–**c3**), e.g. $[(Me_4N)_2(CuCN)_2MoS_4]_n$ **c1** [18] which can be regarded as **m4** type units connected by cyano bridges at one end of them to form a zigzag $Cu\cdots CN–Cu\cdots CN$ chain. The nest unit **m7** can also be connected via CN^- bridges at two unsaturated M′ positions to form a zigzag chain, such as $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ and $[WOS_3Cu_3(CN)(py)_4]_n$ **c2** [19]. When two X groups of the secondary building block **o2** are substituted by two η^5-C_5Me_5 groups the derivative block **o2** can use its two unsaturated Ag atoms to coordinate with μ-CN and connect further to each other to form a zigzag chain. The corresponding cluster is $\{[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_3(CN)\}_n$ **c3** [20].

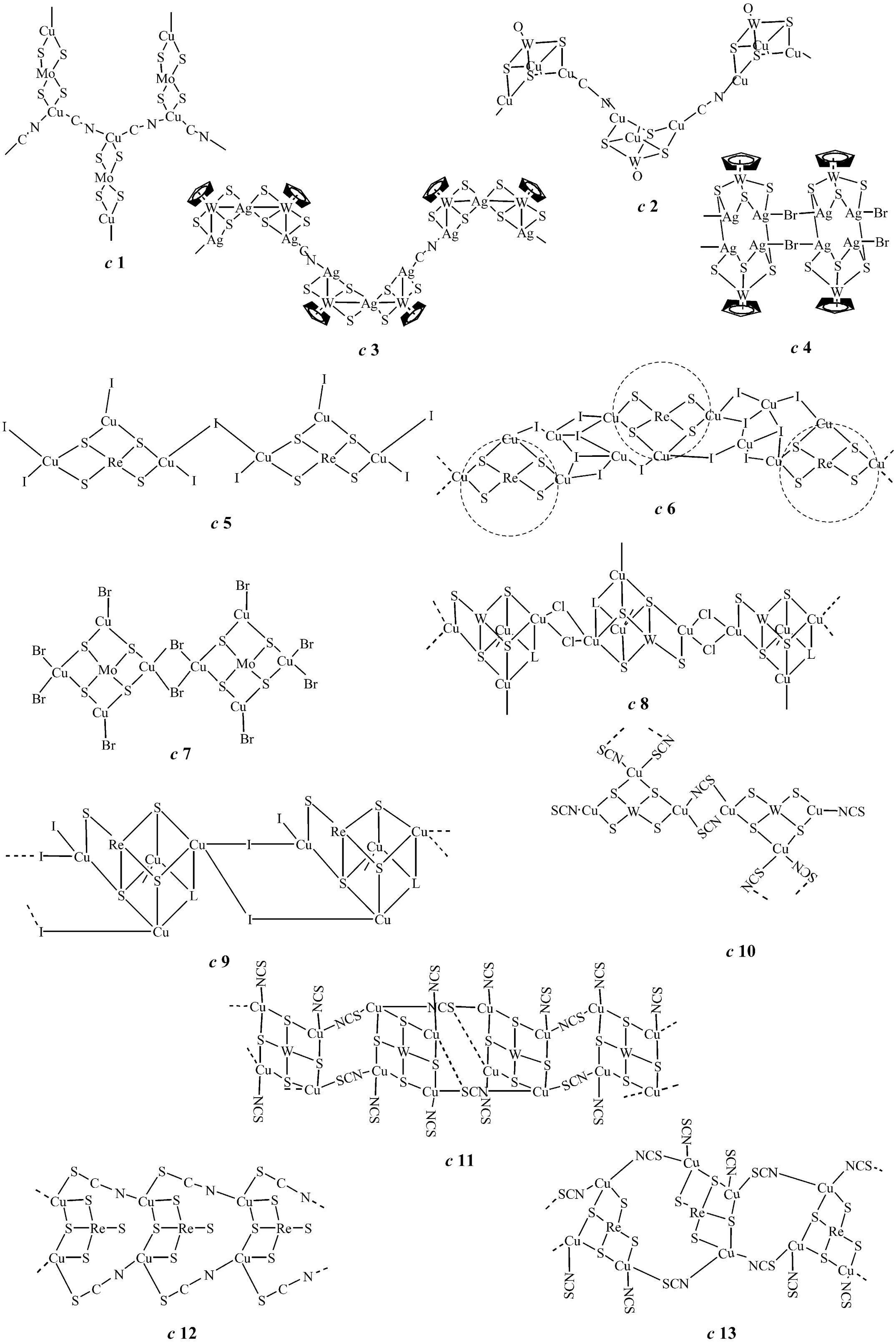
Halide ligands show a preference to form linear structures (Fig. 5, **c4–9**). In the butterfly-shaped **m5**, on substituting X by η^5-C_5Me_5, two of these special blocks can coexist in the dimeric cluster $[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_4$, which can further be linked by doubles of μ_2-Br to generate a ladder polymer $[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br]_n$ **c4** [21]. The unit **m6** can polymerize through iodide bridges to its two M′ at opposite sites to form a linear chain cluster $\{[NEt_4]_2[(ReS_4)Cu_3I_4]\}_n$ **c5**. In addition, cluster junctions and metal junctions may coexist in one polymeric chain, e.g. **m6** and Cu^+ can polymerize with iodide bridges to generate the compound $\{[NPr_4]_2[ReS_4Cu_5I_6]\}_n$ [22] with the double chain structure **c6** (cluster units marked with dashed circles), which can also be described as the result of connected CuI_4 tetrahedra sharing edges or corners, where every sixth CuI_4 tetrahedron is replaced by an ReS_4 tetrahedron. The square block **m11** is connected via two μ_2-Br ligands at two diagonal Cu atoms to form a one-dimensional polymer $[PPh_4]_2[MoS_4(CuBr)_4]\cdot Me_2CO$ **c7** [23], which can be regarded as an extended motif of **o7**. The pentanuclear cubane **m12** (with an additional face) has two polymerization options along the extending direction of the additional face: head to head, such as $\{[NPr_4]_2[WS_4(CuCl)_4]\}_n$) and $[Cu_4Cl_2BIPy_2WS_4]_n$ **c8** [24], or head to tail, such as $[(PPh_4)_2(ReS_4)Cu_4I_5]_n$ **c9** [25].

Thiocyanate groups tend to form dimer-based chains (Fig. 5, **c10–11**). At two M′ positions the incomplete square blocks **m6** are connected via two μ-NCS to form the zigzag polymeric cluster $\{(NEt_4)_2[(CuNCS)_3WS_4]\}_n$ ***c*10** [26]. The square block **m11** can also be connected alternately at two neighboring or opposite Cu atoms via pairs of μ-NCS or μ_3-NCS ligands to form the dimer-based chain cluster $\{[NEt_4]_3[Cu_4(NCS)_5WS_4]\}_n$ ***c*11** [26]. The cause of formation of these chain structures was explored firstly via the excision of the three-dimensional solid $[CuNCS]_n$ with $ReS_4{}^-$ groups, thus creating two polymeric clusters with interesting strand motifs $\{(PPh_4)[(ReS_4)Cu_2(NCS)_2]\}_n$, $\{(NEt_4)_2[(ReS_4)Cu_3(NCS)_4]\}_n$ (**c12–13**) [27], which can be regarded as **m5** or **m6** bridged by two μ-NCS groups. The nature of the resulting products is in any case strongly influenced by the relative overall amounts of reactants and the type of solvents used.

2.2.2. Skeletal S ligand-bridging self-assemblies

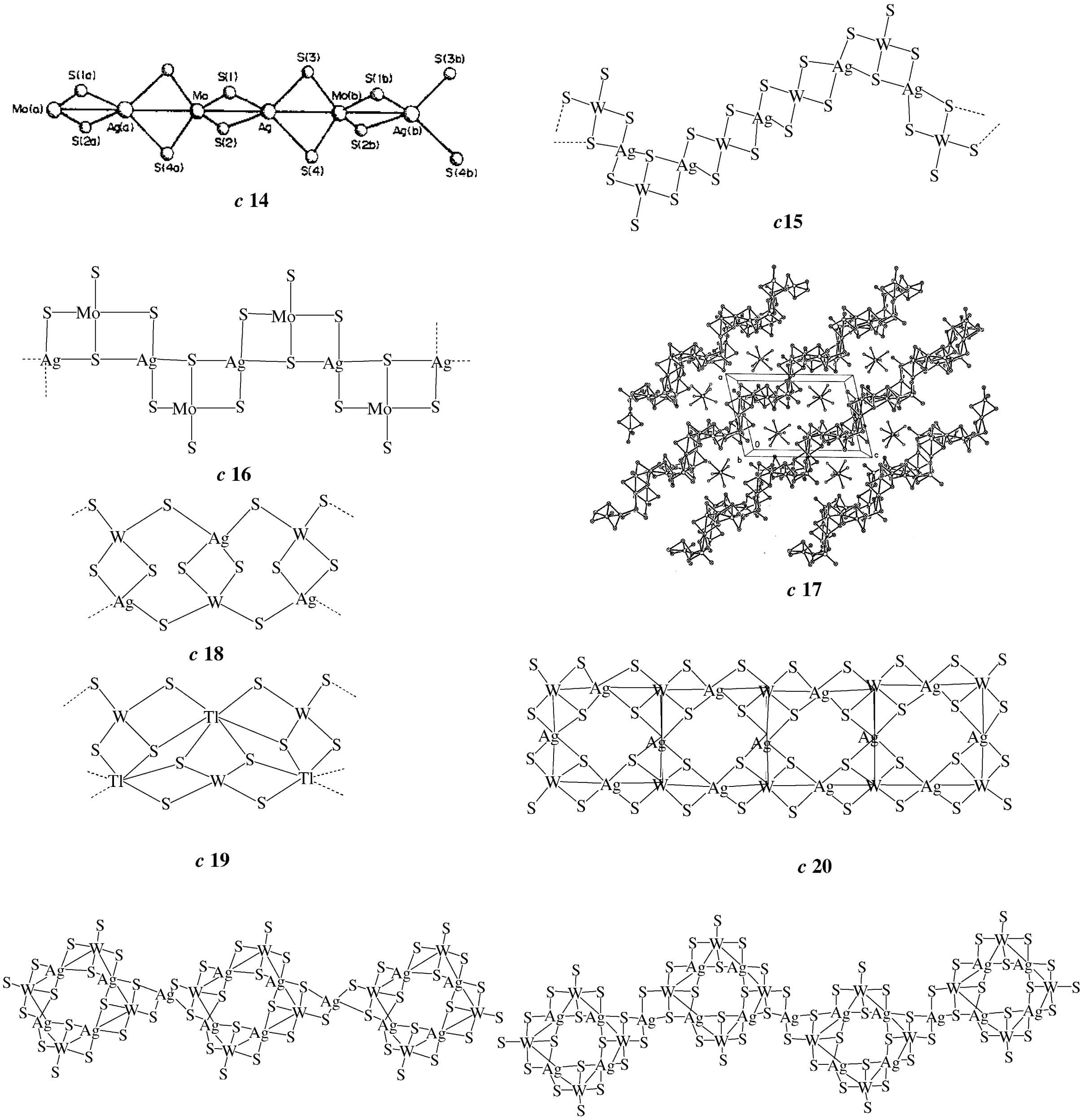
The known sulfur-containing ligands show a surprising variety of coordination types, including mainly *t*-S, μ-S, μ_3-S and μ_4-S, etc. It has been discussed that the reactivity of terminal M–S groups is higher compared to that of bridging M–S–M ones and a decrease in the negative charge on S is observed (t-S > μ-S > μ_3-S) [6]. The coordination means of the sulfido ligands plays an important role in determining the coordinating behavior of the thiometalato ligand $MS_4{}^{2-}$(Fig. 6, **c14–22**). A strong absorption band in the (resonance) Raman spectrum of $\{[(C_6H_5)_4P]AgMoS_4\}_n$ inferred a polymeric structure [28]. As expected this point was testified later via the determination of the crystal structures of the polymeric species $[AgMS_4\cdot\gamma\text{-}MePyH]_n$ and $[AgMoS_4\cdot\alpha\text{-}MePyH]_n$ (M = Mo, W) [29a] **c14**. These clusters can be described as linear assemblies based on block **m1** with Ag extending along an $M\cdots Ag$ axis. Compared with discrete cluster units, shorter M–Ag distances (2.90–2.95 Å) indicate a stronger intrachain metal–metal interaction. Other polymers belonging to this category include $[Cu(NH_4)MoS_4]_n$ [29b], $[(AgWS_4)X]_n$ (X = $NH_3C(CH_2OH)_3\cdot 2DMF$ [29c], NH_4 [29d], or $Li(DMF)_4$ [29e]) and $[(PPh_4)AgMoS_4]_n$ [29f].

When block **m1** connects silver atoms simultaneously along the bimetal nuclear axis and the vertical direction, a one-dimensional polymer $[W_4S_{16}Ag_4\cdot 2Ca(DMSO)_6]_n$ **c15** showing a zigzag chain is formed [30]. Polymerization turns a simple *t*-S into corner μ-S, and a μ-S turns into corner μ_3-S. The short edges (W_2Ag) and long edges (W_4Ag_3) are approximately alternately perpendicular to each other. **m1** assembles with two *cis*-Ag to form the zigzag polymeric cluster $[Ca(DMF)_6Mo_2Ag_2S_8]_n$ **c16** [31]. Remarkably **m1** can even assemble with Ag^+ to form a polymeric helical chain configuration in polymers $\{[M_3Ag_3Q_{12}][M'(Me_2SO)_8]\}_n$ (M = Mo, W; Q = S, Se, M′ = La, Nd) **c17** [32], in which each Ag atom forms a more distorted tetrahedron comprising two μ_2-S and two μ_3-S. Each M′(III) atom is coordinated by the O atoms of eight DMSO ligands. The large trivalent cations $[M'(Me_2SO)_8]^{3+}$ are located among the anionic helical chains and well separated from each other and the anion chains. In all these examples, cluster units function as connectors. Interestingly, some of these units can also assemble with each other, acting as both polymeric junctions and linking ligands. For example, when block **m2** interconnects only along the vertical direction of bimetal nuclear axis,



c 1 **c 2** **c 3** **c 4** **c 5** **c 6** **c 7** **c 8** **c 9** **c 10** **c 11** **c 12** **c 13**

Fig. 5. Thirteen peripheral ligands (CN, Cl, Br, I, NCS) bridging assemblies.



c 14

c15

c 16

c 17

c 18

c 19

c 20

c 21

c 22

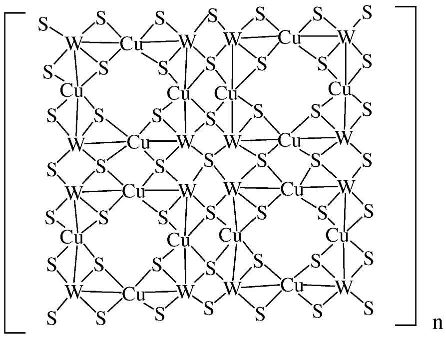
Fig. 6. Skeletal S ligands (*t*-S, μ-S, μ_3-S) bridging assemblies.

the product obtained $[WS_4Ag{\cdot}NH_3C(CH_2OH)_3{\cdot}H_2O]_n$ **c18** [33] shows a composite double chain polymeric structure. Its structure can also be regarded as two –S–W–S–Ag– zigzag chains connected through μ-S doubles. All sulfur bridges between two chains still possess coordination reactivity. Like supramolecular species, the heterometal coordination preference and the orientation geometry of sulfur ligands provide the assembly instructions [1c]. When tetrahedrally coordinated Ag atoms are replaced by octahedrally coordinated Tl atoms, all intrachain μ-S bonds turn further into μ_3-S, e.g. the M–S–Tl polymeric cluster $\{[(N\text{-}Bu)_4N][TlMS_4]\}_n$ **c19** [34] (M = Mo, W). The diversity of the M–S–Ag chains mentioned above indicates that the cation moiety or guest molecule has a strong impact on the host cluster framework.

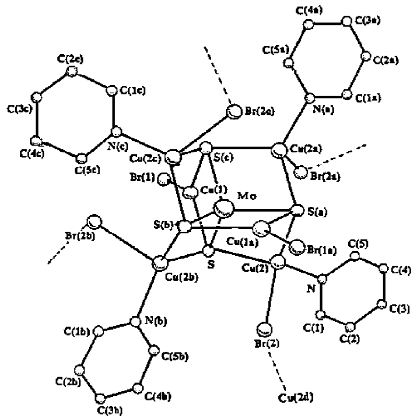
The octanuclear square block **o5** provides three kinds of construction mode through sharing Ag atoms at different positions, e.g. $\{[W_4Ag_6S_{16}]X\}_n$ (X = $[Ca(DEAC)_6]^{2+}$ or $[n\text{-}Bu_4N]_2{}^{2+}$), $\{[W_4Ag_5S_{16}][M(DMF)_8]\}_n$ (M = Nd, La) and $\{[W_8Ag_{10}S_{32}][La(DEF)_8]_2\}_n$ **c20**–**22** [35]. Polymerization turns simple *t*-S in **o5** into μ-S, and μ-S into μ_3-S.

2.3. Two-dimensional polymeric clusters

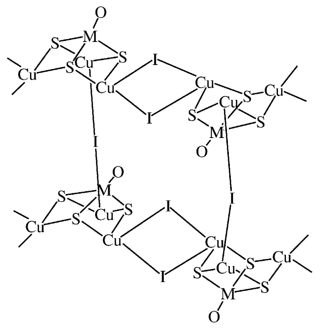
Another intriguing example related to **o5** is the layered sulfide $[Cu_2WS_4]_n$ **s1** (Fig. 7), which can be considered as a



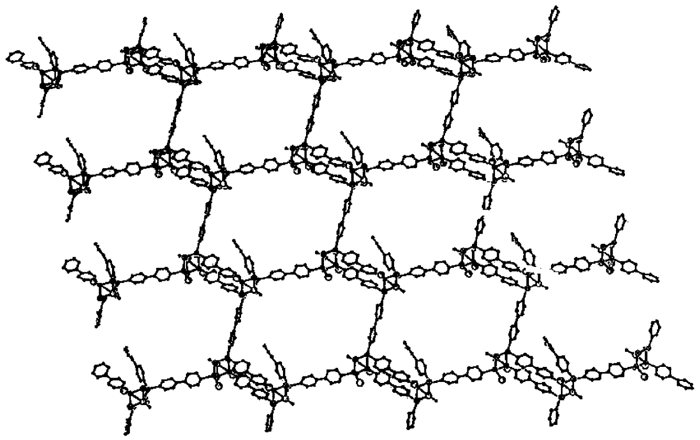
s **1**



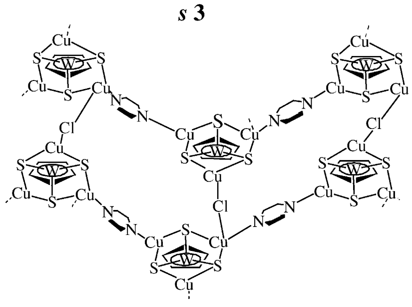
s **2**



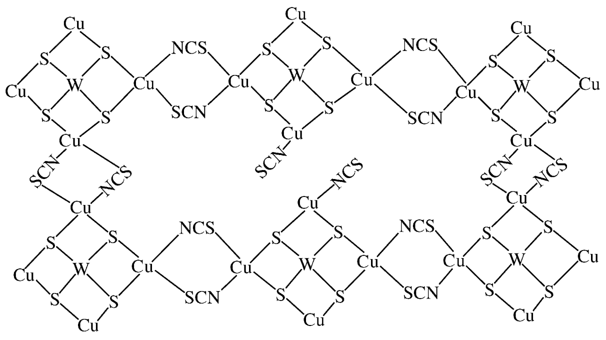
s **3**



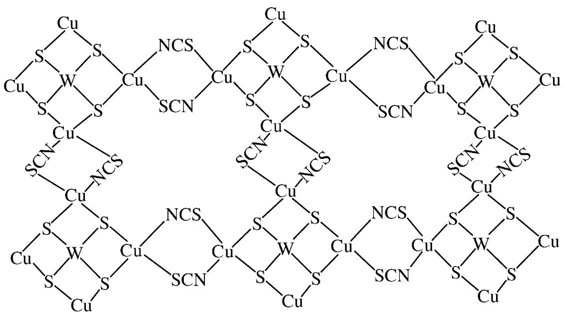
s **4**



s **5**



s **6**



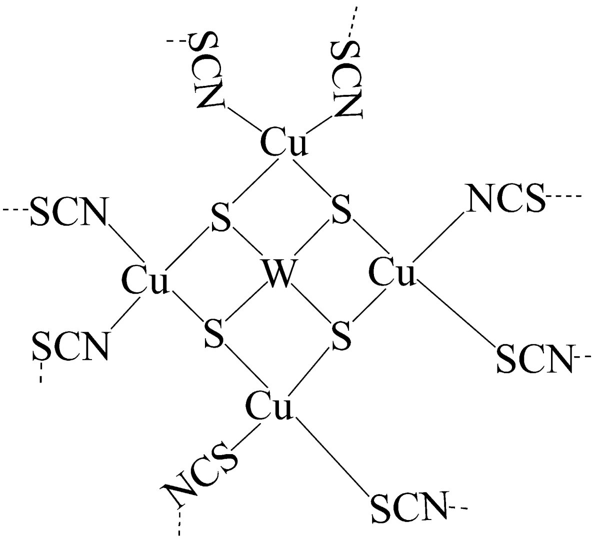
s **7**

Fig. 7. 2D polymeric clusters.

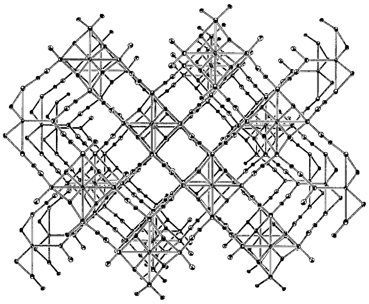
sheet-by-sheet product where the octanuclear square blocks **o5** extend and polymerize with each other in diverse directions. All *t*-S and μ-S are thus turned into μ_3-S. There are only weak van Der Waals interactions between these layers [36]. Blocks **m14** connect with each other at four equatorial Cu atom positions through μ_2-X (X = Br, I) groups to form the two-dimensional sheet products $[MoS_4Cu_6X_4py_4]_n$ **s2** [37] (X = Br, I; py = pyridine). **m7** interact each other via I_2 double bridges and μ-I to produce a novel 2D motif $\{[NMe_4]_2[MOS_3Cu_3(\mu_2\text{-}I)_3]\}_n$ ***s*3** (M = Mo, W) [38]. We also employed **m7** and 4,4'-bipyridine to construct another 2D motif $\{[Mo_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_5]\cdot H_2O\}_n$ **s4** [39] by a rational two-step assembly. Derivative blocks **m7** (X $=\eta^5$-C_5Me_5) can be connected with each other at three Cu positions via pyrazine or chloride ligands to form the 2D sheet structure product $\{[(\eta^5\text{-}C_5Me_5)WS_3Cu_3Cl(MeCN)(pz)](PF_6)\}_n$ (pz = pyrazine) **s5** [40]. The pentanuclear square block **m11** can share doubles of μ-NCS attached on neighboring or opposite Cu atoms to form a sheet based on six-membered motifs, e.g. $\{(PPh_4)_2[(CuNCS)_4WS_4]\}_n$ **s6** [41]. Interestingly, under Cu···S (NCS) weak interaction, the two central three-coordinated copper atoms approach to achieve a pseudo-tetrahedral coordination, and thus another two-dimensional compound $\{[NEt_4]_2[(CuNCS)_4WS_4]\}_n$ **s7** based on the more compact four-membered motif is formed [26].

2.4. Three-dimensional polymeric clusters

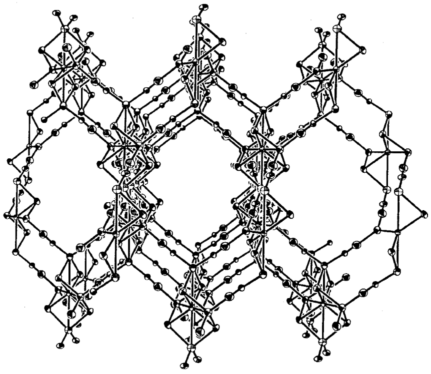
So far, all 3D frameworks of the polymeric clusters discussed here are dominated by the pentanuclear square block **m11**. An earlier example is the NCS-bridging polymer $\{(NMe_4)_2[(CuNCS)_4WS_4]\}_n$ **n1** [42] (Fig. 8) in which a three-dimensional network comprising solely four-coordinated copper atoms is observed. Due to the variations of Cu-NCS and Cu-SCN angles the overall assembly shows no particular directionality or layering. Based on structures related to **m11**, we envisaged that it could be explored as an efficient candidate for the synthesis of polymeric species. In order to demonstrate that **m11** is an attractive building block for polymeric systems, we employed CN^- as the bridging ligand to generate the three-dimensional polymers $\{[Et_4N]_2[(MS_4)(CuCN)_4]\}_n$ [32b,43] **n2** (M = Mo, W; X = S, Se) (see, Fig. 8, **n2a**–**b** for the results of the X-ray crystal structure analysis of **n2**). In contract to **n1**, in **n2** the **m11** units bridged via the cyanide ions are slightly bent with Cu–C–N angles



***n*1**



***n*2a**



***n*2b**

Fig. 8. 3D polymeric clusters with **m11** as construction unit. (**n**2a) View of the 3D cross-framework of clusteric anion along the *c* axis. (**n**2b) Perspective view of the 3D channel viewed along the *c* axis. The diameter of the inner cavities is ca. 1.3 nm.

$= 175.6(9)^\circ$ and Cu–N–C $=174.5(10)^\circ$. The cyanide ligands function as nearly linear bridges between **m11** units and thus a cross-framework configuration is formed. The **m11** units bridged by cyanide ligands extending along the *c* axis, give rise to fascinating hexagonal nanosized channels (**n2b**) which provide cavities of sufficient size, capable of accommodating $[Et_4N]^+$ cations necessary to balance the cluster anions.

3. General structural features

Fifty-five heterothiometallic clusters and 40 polymeric structural types (including nine 0D structures, 22 1D structures, 7 2D structures, 2 3D structures) have been illustrated above. In accordance with our previous classification, several general features of heterometallate polymeric clusters can be summarizedas follows.

1. Construction blocks with higher symmetry display an increased tendency for polymerization. For example the pentanuclear square block **m11** ($[M'_4MS_4]^{2+}$) can result in zero-dimensional ($[(PPh_4)_4][WS_4(CuCl)_4]_2$ **o7** [15]), one-dimensional ($[PPh_4]_2[MoS_4(CuBr)_4]\cdot Me_2CO$ **c7** [23], $\{[NEt_4]_3[Cu_4(NCS)_5WS_4]\}_n$ **c11** [26]), two-dimensional ($\{(PPh_4)_2[(CuNCS)_4WS_4]\}_n$ **s6** [41], $\{[NEt_4]_2[(CuNCS)_4WS_4]\}_n$ **s7** [26]), and three-dimensional structures($\{(NMe_4)\ [(CuNCS)_4WS_4]\}_n$ **n1** [42], $\{[Et_4N]_2[(MS_4)(CuCN)_4]\}_n$ [43,32] **n2**) via bridging; the octanuclear square block **o5** exhibits its polymerizing diversity by S-coordination in different positions ($\{[W_4Ag_5S_{16}]\}_n[M(DMF)_8]_n$ (M $=$ Nd, La), $\{[W_4Ag_6S_{16}][Ca(DEAC)_6]\}_n$ and $\{[W_8Ag_{10}S_{32}]\}_n$ $\{[La(DEF)_8]_2\}_n$ **c20–22** [35] and $[Cu_2WS_4]_n$ **s1** [36]).
2. Obviously during polymerization the connection mode of the ligand tends to complication. Among the known bridging ligands, S, Cl, Br, and/or I, NCS tend to bind with cluster blocks to form four-membered rings of the double-bridge type (such as ($[Et_4N][PNP]_2[Co(WS_4)_2]$ $2CH_3CN$ [10]) **o1**, or **o7**, **o8**, **c7**, **c8**, **c10**; **s2**, **s6**, **s7**, etc.), whereas the CN^- ligand tends to polymerize via a single bridge (such as $\{(Me_4N)_2[(CuCN)_2MoS_4]\}_n$ **c1** [18], or **c2**, **c3** and **n2**). Regarding the S ligand, polymerization leads to connection transformation in the order: *t*-S → μ-S, and μ-S → μ_3-S (such as ($[Et_4N][PNP]_2[Co(WS_4)_2]2CH_3CN$ [10]) **o1**, or **c14–c22** and **s1**).
3. Cluster construction blocks show common characteristics, both electron donating (*t*-S, μ-S, μ_3-S) and electron accepting (M′), thus can act as cluster junctions in peripheral ligand-assemblies (such as $[(PPh_4)_4][WS_4(CuCl)_4]_2$ **o7** [15], or **o8**, **c1–c13**, **s2–s7**, **n1** and **n2**), while in the sulfur-assembly mode, they may be cluster rods or spacers (such as $[AgMS_4MePyH]_n$ [29a] **c14**, or **c15–c22** and **s1**).
4. In supramolecular architectures, the change in dimensions induced by the guest molecules or counterions is a well-known phenomenon. Among polymeric clusters, the packing density tends to loosen with increasing cation size, i.e. the so-called size effect of counterions [26]. For example using the same assembly components, when the large cation $[Ph_4P]^+$is used, the monomeric $\{[Ph_4P]_2(CuCN)_2MoS_4\}$ is obtained, using the smaller cation $[Me_4N]^+$, polymeric $\{[Me_4N]_2(CuCN)_2MoS_4\}_n$ is obtained [18]. Another especially remarkable example is $\{[NMe_4]_2[Cu_4(NCS)_4MoS_4]\}_n$ (3D, **n1**) → $\{[NEt_4]_2[Cu_4(NCS)_4MoS_4]\}_n$ (2D, **s7**) → $\{[PPh_4]_2[Cu_4(NCS)_4MoS_4]\}_n$(2D, **s6**) [41]. In contrast with the tightly-packed three-dimensional framework compound **n1**, 2D sheets are formed in the latter two polymers. Since $[PPh_4]^+$ is considerably larger than $[NEt_4]^+$, the corresponding sheet structure turns from the compact four-membered motif (**s7**) to the less dense six-membered motif (**s6**).

   From the cation replacement point of view, a change of cation size may give rise to a transformation of the polymeric anion clusters. In DMSO solution, there are two reactions of this type, as shown in Eqs. (1) and (2)

$$\underset{\mathbf{c14}}{\{(PPh_4)_2[AgWSe_4]\}_n} + La(NO_3)_3\cdot H_2O \rightarrow \underset{\mathbf{c17}}{\{[La(Me_2SO)_8][Ag_3(WSe_4)_3]\}_n} \tag{1}$$

   This gradual process has been followed by ^{77}Se NMR spectroscopy [32b].

$$\underset{\mathbf{c14}}{[AgWS_4\cdot HNEt_3\cdot DMF]_n} + Ca(NO_3)_3\cdot H_2O \rightarrow \underset{\mathbf{c15}}{[(AgWS_4)_4\cdot 2Ca(DMSO)_6]_n} \tag{2}$$

   Obviously the cation-size effect puckers the linear structure to produce a helical or zigzag arrangement. Because the organic cations ($[Ph_4P]^+$, $[NEt_4]^+$, $[Me_4N]^+$) can be easily displaced by the larger complex cations ($[La(Me_2SO)_8]^+$, etc.), many novel structural motifs can be anticipated by this kind of displacement.
5. Many organic ligands, which can be conveniently introduced into cluster systems by nucleophilic replacement, exhibit different connecting modes in relation to the inorganic ligands mentioned above. More importantly, because polymeric clusters possess clusteric knots with larger spatial size, larger inner cavities may be obtained. The related porous species of coordination polymer have been the subject of investigation for some time because of their ability to selectively include ions and molecules and catalyze specific chemical transformations [44]. The cavity size of representative macroporous polymeric cluster and the related coordination polymers are listed in Table 1.

Table 1
The cavity size of representative macroporous polymeric cluster and the related coordination polymers

Macroporous compounds	Average cavity diameter (nm)	Refs.
$[(en)Pd(4,4\text{-bipy})]_4(NO_3)_8$	0.78	[45]
$\{[Cd(4,4\text{-bipy})_2](NO_3)_2\}_n$	1.18	[45]
$\{[Mo_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_5]\cdot H_2O\}_n$	2.17	[39]

4. Properties of polymeric clusters

Polymeric clusters are of special interest mainly due to their properties: (i) most polymeric species possess robust thermostability, (ii) all polymeric skeletons exhibit great photostablity toward the photodegradation process associated with terminal ligand substitution by solvents, especially toward the light-induced fragmentation caused by electronic transitions between the skeleton bonding and antibonding orbitals. Both of above features represent a unique opportunity for probing correlations between structure and properties, (iii) results from our recent studies suggest that polymerization could provide an enhancement of optical limiting effects, as illustrated in Table 2.

4.1. Non-linear optical properties

The design and synthesis of new materials with large optical limiting capacity represents an active field in modern physics, chemistry, and material science. Our previous studies show that many monomeric clusters possess strong nonlinear optical absorptive and nonlinear optical refractive properties. For example the planar 'open' skeleton heterothiometallic cluster, $[WS_4Cu_4I_2(py)_6]$ **m11**, exhibits large optical limiting effects. The limiting threshold is as low as 0.07 J cm^{-2}, which is better than those of the known phthalocyanine derivations and C_{60} [47]. Because polymeric clusters possess the combined strength of both clusters and polymers, we conclude that they may exhibit special properties. Both the dimer **o8** and the one-dimensional polymer **c19** exhibits strong NLO absorption and self-focusing effects. The two-dimensional network polymer $[MoS_4Cu_6I_4(Py)_4]_n$ **s2** [37] has the biggest third-order nonlinear absorption index of all inorganic clusters and a very large optical limiting capacity. The three-dimensional cross-framework cluster $\{[Et_4N]_2[(WSe_4)(CuCN)_4]\}_n$ **n2** also have a low limiting threshold of 0.2 J cm^{-1}.

Table 2
Nonlinear optical polymerization effect of heterothiometallate clusters

Clusters	Polymeric types	Limiting threshold (J cm^{-2})[a]	Refs.
$[Et_4N]_2[WS_4Cu_4(NCS)_4(2\text{-pic})_4]$	**m11**	0.3	[46]
$\{[WS_4Cu_4(CN)_4]^{2-}\}_n$	**n2**	0.15	[43]
$[MoOS_3Cu_3BrCl_2]^{2-}$	**m7**	10	[39]
$[Mo_2O_2S_6Cu_6Br_2I_4]^{4-}$	**o8**	2	[39]
$\{[Mo_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_5]\cdot H_2O\}_n$	**s7**	0.4	[39]

[a] The peripheral ligands only have less impact on the NLO properties.

4.2. Electrical properties

Many unconventional semiconductors will become an active research area because of their similar properties to artificial systems of conventional semiconductors, such as $[NH_2C(I)\!=\!NH_2]_3PbI_5$ (3D), $(C_9H_{19}NH_3)_2PbI_4$ (2D) and $(MeNH_3I)_3SnI_5$ (1D) [48]. Some M–Ag–S (M = Mo, W) polymeric systems exhibit semiconductor character, such as $\{[W_2Ag_2S_8][Zn(4,4'\text{-bipy})_2(DMF)_2(DMSO)_2]\}_n[Ca(DEAC)_6]_n$, $\{[W_4Ag_6S_{16}]\}_n[Ca(DEAC)_6]_n$ and $\{[W_8Ag_{10}S_{32}]\}_n[M(DEF)_8]_2\}_n$ ($M = La^{2+}$, Nd^{2+}) [35].

5. Spectra features of polymeric clusters

5.1. Low wave-number region of IR spectra

The IR spectra of monomeric heterothiometallic cluster containing $[MXS_3]^{2-}$ have been systemically studied [7,8,9]. The characteristic ν(M–S) have been proven valuable for the judgement of monomeric cluster skeleton and some oligomeric species constructed by skeletal S ligands [8]. So the related data was not demonstrated again here. The available IR spectral parameters of 1–3 dimensional polymeric compounds mentioned in this review are listed in Table 3.

5.2. High wave-number region of IR spectra

In monomeric M–S–M′ systems, it is well known that after coordination the spectroscopic features of polythiometallate ligands $MXS_3{}^{2-}$ will be greatly modified [7]. For the same reason, in polymer cluster systems, the bridging ligand will show different spectroscopic features from its terminal modes after polymerization. The thiocyanate group was taken as a typical example for the discussion of the IR spectra and the construction of polymeric clusters because its IR spectra have been studied extensively for distinguishing the different bonding modes [41,50]. The ν(CN) stretching frequency is generally observed in the range 2100–2050 cm^{-1} for N-bonded thiocyanate, 2130–2085 cm^{-1} for S-bonded thiocyanate, and 2165–2065 cm^{-1} for bridged NCS groups. The ν(CN) stretching frequency for the related isolated and polymeric clusters are compared in Table 4. A blueshift is observed following polymeric bridging.

6. Syntheses and reactions

6.1. Synthesis approach

The preparative routes to polymeric clusters can be categorized into two major groups: solution reaction and

Table 3
The characteristic IR spectra of heterothiometallic polymeric clusters

Compounds	Blocks	M–S$_t$	M–μ-S	M–μ$_3$-S	Refs.
$(Et_4N)_2MoS_4$	**m1**	470			[49]
$(Et_4N)_2WS_4$	**m1**	458			[49]
$\{[(Me_4N)_2(CuCN)_2MoS_4]\}_n$	**c1**				[18]
$\{[MoOS_3Cu_3(CN)(py)_3]0.5C_6H_6\}_n$	**c2**		441	412	[19]
$[WOS_3Cu_3(CN)(py)_4]_n$	***c*2**			428	[19]
$\{[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_3(CN)\}_n$	**c3**		441	424, 409	[20]
$[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br]_n$	**c4**			435	[21]
$\{[NEt_4]_2[(ReS_4)Cu_3I_4]\}_n$	**c5**		484, 470	447, 439	[22]
$\{[NPr_4]_2[ReS_4Cu_5I_6]\}_n$	**c6**		480	445, 438	[22]
$\{[PPH_4]_2[MoS_4(CuBr)_4]Me_2CO\}_n$	**c7**			472, 458	[23]
$\{[NPr_4]_2[WS_4(CuCl)_4]\}_n$	**c8**			445	[24]
$[Cu_4Cl_2(bipy)_2WS_4]_n$	**c8**		505	470, 438	[24]
$[(PPh_4)_2(ReS_4)Cu_4I_5CH_3CN]_n$	**c9**		488	449, 421	[25]
$\{(NEt_4)_2[(CuNCS)_3WS_4]\}_n$	**c10**		471	461, 444	[26]
$\{[NEt_4]_3[Cu_4(NCS)_5WS_4]\}_n$	**c11**			442	[26]
$\{(PPh_4)[(ReS_4)Cu_2(NCS)_2]\}_n$	**c12**	515			[27]
$\{(NEt_4)_2[(ReS_4)Cu_3(NCS)_4]\}_n$	**c13**				[27]
$\{[W_2Ag_2S_8][Zn(4,4'\text{-}bipy)_2(DMSO)]_4(DMSO)]\}_n$	**c14**		447, 403		[35b]
$\{AgMoS_4\gamma\text{-}MePyH\}_n$	**c14**		445		[29a]
$\{AgWS_4\gamma\text{-}MePyH\}_n$	**c14**		437		[29a]
$[AgMoS_4\alpha\text{-}MePyH]_n$	**c14**		439		[29a]
$[CuNH_4MoS_4]_n$	**c14**		460		[29b]
$[WS_4AgNH_3C(CH_2OH)_32DMF]_n$	**c14**				[29c]
$[AgWS_4NH_4]_n$	**c14**		439		[29d]
$[N(C_6H_5CH_2)(C_2H_5)_3MoS_4Ag]_n$	**c14**		459, 439		[31]
$\{[PPh_4]_2[AgMoS_4]\}_n$	**c14**				[29e]
$[W_4S_{16}Ag_42Ca(DMSO)_6]_n$	**c15**	487	447	412	[30]
$\{[Ca(DMF)_6Mo_2Ag_2S_8]\}_n$	**c16**		455	416	[31]
$\{[W_2Ag_2S_8][Zn(4,4'\text{-}bipy)_2(DMF)_2(DMSO)_2]\}_n$	**c16**	490	442	422	[35b]
$\{[W_3Ag_3S_{12}][Nd(Me_2SO)_8]\}_n$	**c17**	489	439	422, 407	[32]
$\{[W_3Ag_3Se_{12}][La(Me_2SO)_8]\}_n$	**c17**	313	298	288, 280	[32]
$[WS_4AgNH_3C(CH_2OH)_3H_2O]_n$	**c18**				[33]
$\{[(n\text{-}Bu)_4N][TlWS_4]\}_n$	***c*19**		460	447, 434	[34a]
$\{[(n\text{-}Bu)_4N][TlMoS_4]\}_n$	**c19**		551, 460		[34b]
$\{[W_4Ag_5S_{16}]\}_n[M(DMF_8]_n$ (M = Nd, La)	**c20**		441, 424	409	[35a]
$\{[W_4Ag_5S_{16}][La(DEF)_2(DMF)_6][La(DEF)_4(DMF)_4]\}_n$	**c20**	494	473, 461	450, 426	[35d]
$\{[W_4Ag_6S_{16}]\}_n[Ca(DEAC)_6]_n$	**c21**	505	467, 447	436, 417	[35b]
$\{[W_8Ag_{10}S_{32}]\}_n\{[La(DEF)_8]_2\}_n$	**c22**	494	469, 446	420	[35]
$[Cu_2WS_4]_n$	**s1**			443	[36]
$[MoS_4Cu_6Br_4(Py)_4]_n$	**s2**			438	[37]
$\{[NMe_4]_2[MOS_3Cu_3(\mu_2\text{-}I)_3]\}_n$ (M = Mo, W)	**s3**				[38]
$\{[Mo_2O_2S_6Cu_6I_3(4,4'\text{-}bipy)_5]H_2O\}_n$	**s4**		459	434	[39]
$\{[(\eta^5\text{-}C_5Me_5)WS_3Cu_3Cl(MeCN)(pz)]\}PF_6\}_n$	**s5**			429, 407	[40]
$\{(PPh_4)_2[(CuNCS)_4WS_4]\}_n$	**s6**			443	[41]
$\{[NEt_4]_2[(CuNCS)_4WS_4]\}_n$	**s7**		455	435	[26]
$\{[Nme_4][(CuNCS)_4WS_4]\}_n$	**n1**			440	[42]
$\{[Et_4N]_2[(WSe_4)(CuCN)_4]\}_n$	**n2**			294	[32]
$\{[Et_4N]_2[(MoS_4)(CuCN)_4]\}_n$	**n2**			458	[43]
$\{[Et_4N]_2[(WS_4)(CuCN)_4]\}_n$	**n2**			447	[43]

solid state reaction. The preparation of clusters carried out in solution lead to the discovery of many polymeric species involving reaction materials such as thiometallates, M′X (X = NCS$^-$, Cl$^-$, Br$^-$, I$^-$) and some salts (KNCS, NaCN, etc.). Recently, many interesting polymer frameworks have been created using various starting materials, such as heterometal complexes ($[(M'(CH_3CN)_4)BF_4]$, polythiometallocenes such as $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3]$, or some oligometric species. With such synthetic methods, over 40 clusters with 23 different types of polymeric framework have been obtained (**o1**, **o4**, **c1**, **c2**, **c20–c22**, **s1**, **s3**, **s5–s7**, **n1**, **n2**, etc.). Since the publication of the first review on solid state reactions at lower temperatures [5], a break-through in Mo(W)–Cu(Ag)–S(Se) type chemistry has been achieved with the discovery of many novel cluster structures via this approach. The remarkable advantages of this method include low reaction temperatures (mostly below 100 °C), short periods of time, and easy handling.

Table 4
The $\nu|\mathrm{CN}|$ stretching frequency for the related monomeric and polymeric clusters/cm^{-1}

Type	Compounds	60	50	40	30	20	10	2100	Refs.
Monomeric cluster	$(n\text{-}Pr_4N)_2[(CN)CuMoS_4]$					|			[52]
Polymer cluster	$\{(Et_4N)_2[(CuCN)_2MoS_4]\cdot H_2O\}_n$			|					[52]
Monomeric cluster	$(Ph_4P)_2[(CuSCN)_2WS_4]$							|	[26]
Polymer cluster	$\{(Et_4N)_2[(CuSCN)_3WS_4]\}_n$						|		[26]
Monomeric cluster	$(n\text{-}Pr_4N)_2[(CN)AgWS_4]$			|					[52]
Polymer cluster	$\{[(\eta\text{-}C_5Me_5)WS_3]_2Ag_3(CN)\}_n$	|							[20]
Monomeric cluster	$[PPh_4]_2[Cu(NCS)_2MoS_4]$							|	[26]
Polymer cluster	$\{[PPh_4]_2[Cu_4(NCS)_4MoS_4]\}_n$						|		[26]
Polymer cluster	$\{[NMe_4]_2[Cu_4(NCS)_4MoS_4]\}_n$					|			[26]

Particularly noncrystalline precipitates were efficiently circumvented compared to the solution method. Employing this method, about six clusters (**o3**, **o6**, **o8**, **c18**, **s2**, **s4**) with unique polymeric frameworks have been synthesized.

6.2. Cluster excision

Holm and co-workers has found that the low-temperature excision technique and high-temperature dimensional reduction method are two rational approaches for accessing isolated cluster species from extended arrays of nonmolecular solids [51]. Both concepts for releasing clusters from polynuclear or polymeric frameworks are reflected in the reaction of polymeric clusters. In describing the specific disassembling mechanism, we used Holm's nomenclature for highlighting these interesting reactions. An early paradigm was [52]:

$$\underset{\textbf{c14}}{[CuMoS_4]_n^{n-}} + n\mathrm{CN}^- \rightarrow n\underset{\textbf{m2}}{[CuCNMoS_4]^{2-}} \quad (3)$$

The cyano ligands in this binuclear product are easily displaced and thus the isolated small entity can be used for subsequent syntheses.

A second instructive example is

$$\underset{\textbf{c4}}{[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br]_n} + PPh_3 \rightarrow \underset{\textbf{m5}}{[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br(PPh_3)]} \quad (4)$$

Although the polymeric compound **c4** is insoluble in chloroform, addition of PPh_3 to the suspension makes it gradually dissolve. The excision product consists of the fundamental building block **m5**. Strong σ-donor ligands PPh_3 and pyridine could divide the intractable selenide trinuclear cluster into binuclear blocks **m2**. Similarly, the same excision (Eqs. (5) and (6)) yields the following results:

$$\underset{\textbf{c14}}{\{(PPh_4)[AgMoSe_4]\}_n} + PPh_3 + Ph_4PBr \rightarrow \underset{\textbf{m9}}{[Ag_3MoSe_4(PPh_3)_3Br]} \quad (5)$$

$$\underset{n2}{\{[Et_4N]_2[(WSe_4)(CuCN)_4]\}_n} + \mathrm{py} \rightarrow \underset{m11}{[(WSe_4)Cu_4CN_2(py)_4]} \quad (6)$$

In short, cluster excision may produce monomeric entities from the polymeric cluster systems. This kind of dimensional reduction can be considered as an adverse process of block assembly.

7. Summary and outlook

In the present review, the structural diversity of the classified heterothiometallate polymeric clusters was illustrated with emphasis on the results of the last decade. The chemistry presented here not only deals with the means by which chemists can understand the heterometallate polymeric cluster species but also should stimulate further research in this area whereby novel synthetic and structural methodology could be employed until rational controlled assembly can be achieved. Owing to the comparability of various construction units in different polymeric species [1b], the rules we present here may extend beyond the boundary of heterothiometallic polymeric clusters. In cluster systems the extensive coordinate unsaturation may imply that vacant coordination sites are available for interaction with a wide variety of multifunctional ligands. From this point of view, the chemistry of polymeric clusters possesses considerable promise. It is evident that many potential polymer species have not been invented, especially polymeric clusters with sheets or networks which are still less well understood compared to those of the catena type. Due to the heavy-atom effects, a finite list of Se-containing polymeric clusters is expected to have better NLO properties than similar S-containing ones. Hence, a further challenge will be to scale up the production of the high-dimensional and Se-containing polymeric clusters.

In addition, the high stability of polymeric clusters compared with isolated clusters make them good candidates for solid state catalysis. In plain terms, the development in both cluster chemistry and polymer chemistry has offered great opportunities in the design and construction of many elaborate polymeric cluster systems, with increasing utilization in different areas of applied science.

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